

Perchlorate is Not a Common Contaminant of Fertilizers

W. J. Hunter

Author's address: Dr W. J. Hunter (E-mail: jhunter@lamar.colostate.edu), USDA-ARS, PO Box E., 301 S. Howes St., Fort Collins, CO 80522, USA

With 2 figures and 1 table

Received April 9, 2001; accepted July 2, 2001

Abstract

Perchlorate consumption can cause mental retardation and tumour formation in humans. Recent suggestions that perchlorate may be present as a contaminant in fertilizers and fertilizer components have caused concern in the fertilizer industry. The present study developed methods for improving the HPLC analysis of perchlorate and used these methods to survey 15 US fertilizers for perchlorate. Extraction with 50 mM NaOH rather than water was found to improve extraction efficiency from 84 to 98%. The incorporation of $\text{Ca}(\text{HO})_2$ into the extraction medium to yield 1 : 0.5 or 1 : 1, SO_4^{2-} : Ca^{+2} molar ratios reduced the analytical interference caused by SO_4^{2-} by reducing the slope of the SO_4^{2-} peak tail by ~75%. The study found no perchlorate in any of the fertilizers investigated.

Key words: crop contamination — groundwater — pollution — water quality

Introduction

The perchlorate anion (ClO_4^-) is similar to iodine in both charge and ionic radius. Thus, ingestion of perchlorate presents a health concern because it interferes with the proper functioning of the thyroid gland, which can result in mental retardation in infants and unborn children and thyroid tumours (Renner 1998, 1999a). The proposed human health oral risk benchmark for ClO_4^- is $0.0009 \text{ mg kg}^{-1} \text{ day}^{-1}$ (US EPA 1999). This is the amount that should not cause harm to humans, including sensitive subpopulations, if consumed daily over a lifetime. Most environmental research on ClO_4^- has concerned its presence and persistence in groundwater and the health effects of consuming contaminated water. A recent draft US EPA proposal has recommended that water used for human consumption contain less than $32 \mu\text{g l}^{-1}$ ClO_4^- (Renner 1999b). Little is known about ClO_4^- in plant systems. Plants do take up ClO_4^- and can

concentrate the ClO_4^- in their leaves. Urbansky et al. (2000b) detected ClO_4^- at $5\text{--}6 \text{ mg kg}^{-1}$ in the twigs and 300 mg kg^{-1} in the stalks of salt cedar (*Tamarix ramosissima*) growing in a contaminated streambed. Nzungu et al. (1999) found ClO_4^- levels as high as 2000 mg kg^{-1} in the leaves of willows grown hydroponically on media initially containing $\sim 100 \text{ mg l}^{-1}$ ClO_4^- . There is also preliminary evidence that crops such as lettuce accumulate ClO_4^- up to 0.001% of wet weight (Renner 1999a). However, at present, there is relatively little additional information available about the ability of agricultural crops to concentrate ClO_4^- or on the health effects resulting from the consumption of crops exposed to ClO_4^- .

Fertilizer components can contain ClO_4^- as a natural contaminant. Perchlorate is a natural impurity in Chilean caliche at levels that are high enough to adversely affect sensitive crops (Schilt 1979, Nzungu et al. 1999, Susarla et al. 1999, Urbansky et al. 2000a). Also, ClO_4^- may be a contaminant of some commercial potash (Susarla et al. 2000). In 1999, Susarla et al. reported the results of a survey of several US fertilizers, finding that almost all fertilizers and fertilizer components were contaminated with ClO_4^- . These results suggested that ClO_4^- was more common in fertilizers than previously suspected. However, while many of these claims were later retracted (Susarla et al. 2000), the initial report has created widespread concern within the fertilizer industry. This concern was justified as, due to the large and widespread use of fertilizers, the presence of even small amounts of ClO_4^- would represent a significant source of crop and environmental contamination.

Due to the importance of this question, and the confusion created by the initial report by Susarla et al. (1999), I conducted my own survey analysing

several locally available agricultural, horticultural and specialty fertilizers for ClO_4^- . In addition, as there is currently no standard method for the extraction and analysis of ClO_4^- from solid media (The Weinberg Group Inc. 1999), I evaluated the use of dilute NaOH to extract ClO_4^- , the use of $\text{Ca}(\text{OH})_2$ in a method for removing excess SO_4^{2-} , and the use of an HPLC equipped with an electrochemically regenerated solid-phase suppresser and a methacrylate based quaternary amine column as a means of measuring ClO_4^- in fertilizer.

Materials and Methods

Instrumentation

An HPLC equipped with Peek (polyetherether ketone) lines and components, a 50×4.6 mm anion exchange column (Allsep, Alltech, Deerfield, IL), an autosuppressor (ERIS 1000, Alltech, Deerfield, IL) and a conductivity detector (CDD-6A, Shimadzu, Kyoto, Japan) was used for the analysis. The injection volume was 200 μl and the elution buffer was 3.4 mM NaHCO_3 and 3.6 mM Na_2CO_3 supple-

mented with 0.5 mM p-cyanophenol pumped at 2 ml min^{-1} . This procedure was a modified Alltech method.

Extraction of perchlorate from fertilizers

Three extraction methods were used during the study. For all of these extractions fertilizer samples were initially ground to a fine powder with a mortar and pestle.

For studies involving the influence of NaOH on ClO_4^- recovery, 50 mg of ground Hi Yield Garden Fertilizer (Voluntary Purchasing Groups, Inc., Bonham, TX) was spiked with sufficient ClO_4^- stock solution to yield a 20-mg kg^{-1} final ClO_4^- concentration in the fertilizer. These samples were then shaken with 5 ml of the indicated NaOH solution for 48 h on a rotary shaker operated at 140 r.p.m. After extraction, samples were vortexed for 10 s, and an aliquot of the vortexed sample was pipetted into a microcentrifuge tube and spun at 20 000 g for 10 min at 4°C. A sample of the supernatant fluid was filtered through a 0.45- μm nylon filter (Alltech) for HPLC analysis.

For studies on the reduction of the SO_4^- peak tail, 200 mg of All American Ammonium Sulfate Fertilizer (Purcell Industries, Sylacauga, AL) was spiked with ClO_4^- and shaken

Table 1: Fertilizers analysed for perchlorate

Fertilizer	N-P-K	Manufacturer and location
Super Crop Urea	46-0-0	American Pride Co-op Henderson, CO
Super Crop Ammonium Nitrate	34-0-0	American Pride Co-op Henderson, CO
Super Crop Fertilizer	18-46-0	American Pride Co-op Henderson, CO
Phillips 66 Ammonium Nitrate	33.5-0-0	Phillips Petroleum Co. Bartlesville, OK
All American Ammonium Sulfate	21-0-0	Purcell Industries Sylacauga, AL
All American Ammonium Phosphate	16-20-0	Purcell Industries Sylacauga, AL
All American Lawn & Garden	16-16-16	Purcell Industries Sylacauga, AL
American Green Crab-grass Plus Lawn Food	12-3-5	Purcell Industries Sylacauga, AL
American Green Garden Fertilizer	5-10-5	Purcell Industries Sylacauga, AL
Mountain States Lawn Food	27-3-3	Green It Turf Products Denver, CO
Scotts Turfbuilder	27-3-4	Scotts Co. Marysville, OH
Hi-Yield Garden Fertilizer	8-10-8	Voluntary Purchasing Groups, Inc. Bonham, TX
Ortho RosePride	8-12-4	Solaris Group – Monsanto Company San Ramon, CA
Peters Professional	12-36-14	Scotts Co. Marysville, OH
Stern's Miracle-Gro	15-30-15	Stern's Miracle-Gro Products, Inc. Port Washington, NY

in 20 ml of 50 mM NaOH as described above. Aliquots of this mixture were then mixed with 0, 6.5 or 12.5 mg of $\text{Ca}(\text{OH})_2$ (to yield 1 : 0, 1 : 0.5 or 1 : 1 $\text{SO}_4^- : \text{Ca}^{+2}$ molar ratios) and allowed to incubate for 1 h. After the incubation the samples were vortexed and a subsample withdrawn and filtered for HPLC analysis. Similar studies were conducted using $\text{Ba}(\text{OH})_2$ in place of $\text{Ca}(\text{OH})_2$.

For the analysis of fertilizer samples for ClO_4^- , 50 mg of fertilizer (Table 1) was placed into a 50-ml tube and extracted into 5 ml of 50 mM NaOH solution. With each fertilizer six replicate samples were analysed; three of the replicate samples were spiked with sufficient ClO_4^- stock solution to yield a final concentration of 200 mg kg^{-1} and three received no spike. All samples were incubated for 48 h on a rotary shaker operated at 140 r.p.m. After extraction, 2.0 ml of the sample was mixed with 5 mg $\text{Ca}(\text{OH})_2$ on a vortex mixer. These samples were allowed to sit for 1 h and vortexed again, and a subsample was collected and filtered for HPLC analysis.

Results and Discussion

Extraction of perchlorate from fertilizer with NaOH

Most environmental studies with ClO_4^- have involved its determination in aqueous samples;

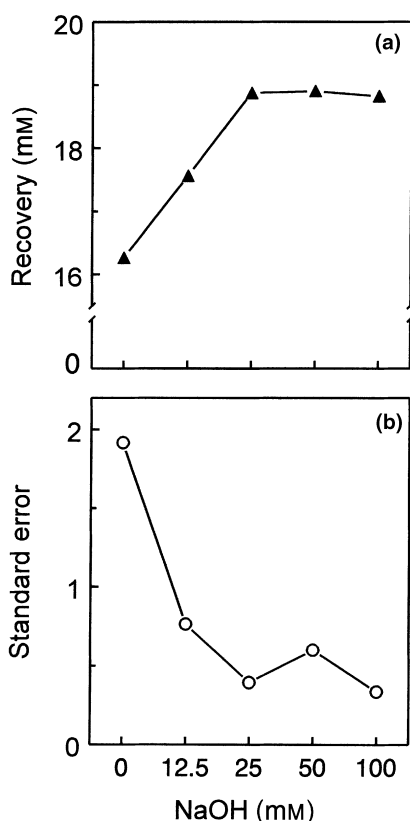


Fig. 1: Influence of NaOH extraction on perchlorate recovery (a) and standard error of the mean (b) of fertilizer samples spiked with perchlorate. Values are an average of three independent measurements

very few have involved the extraction of ClO_4^- from solid material. In most of these studies water was used as the extraction medium (Susarla et al. 1999, 2000). When water alone was used to extract spiked samples, only 84% of the ClO_4^- added to the fertilizer was recovered. However, recovery was improved by the addition of NaOH to the extraction fluid with the highest recovery efficiencies, 97–98%, occurring when 50 and 100 mM NaOH was used to extract ClO_4^- (Fig. 1a). In addition, the standard error of the mean associated with replicate extractions improved as the amount of NaOH present in the extraction medium increased. The least error occurred when 100 mM NaOH was used (Fig. 1b).

Removal of SO_4^{2-} with $\text{Ca}(\text{OH})_2$

With anion exchange columns, SO_4^{2-} elutes shortly before ClO_4^- , and when samples contain large amounts of SO_4^{2-} the tail of the peak can interfere with the detection and integration of the typically much smaller ClO_4^- peak. In such situations, ClO_4^- appears as a small trailing peak on the back of a much larger SO_4^{2-} peak. This can interfere with peak integration. In order to reduce this interference a treatment in which $\text{Ca}(\text{OH})_2$ was added to precipitate a portion of the sulphate present in the samples was evaluated. When $\text{Ca}(\text{OH})_2$ was included in the extraction mixture there was a significant, ~75%, reduction in the slope of the tail of the SO_4^{2-} peak at the point where ClO_4^- elutes (Fig. 2).

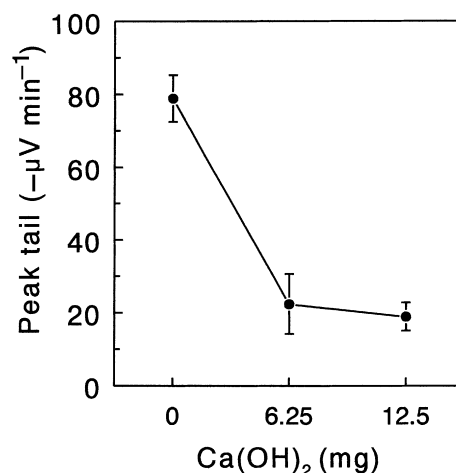


Fig. 2: Reduction in the slope of the SO_4^{2-} peak tail at the point where ClO_4^- elutes by the addition of $\text{Ca}(\text{OH})_2$ to the fertilizer extract. $\text{Ca}(\text{OH})_2$ was added to the extract in the amounts indicated and the extracts were vortexed, filtered and analysed. Values are the mean of three independent measurements \pm SEM

$\text{Ba}(\text{OH})_2$ was found to reduce the slope of the SO_4^{2-} peak tail in a similar manner (data not shown).

Analysis of fertilizer samples for perchlorate

With an injection volume of 200 μl the detection limit of the equipment used was $\sim 20 \mu\text{g kg}^{-1}$. At this detection limit, no detectable ClO_4^- was present in any of the 15 unspiked fertilizer samples examined (Table 1). The ClO_4^- spike was recovered from all of the spiked fertilizer samples. Based on this survey, it is concluded that ClO_4^- is not a common contaminant of fertilizers manufactured in the United States. The results of this study and the conclusions reached clearly disagree with those of Susarla et al. (1999), which implied that ClO_4^- is a common contaminant of US fertilizers, but do agree with those of Susarla et al. (2000) and Urbansky et al. (2000a).

Zusammenfassung

Perchlorat ist keine allgemein auftretende Verunreinigung von Düngern

Perchlorataufnahme kann mentales Zurückbleiben und Tumorbildung bei Menschen verursachen. Unlängst vorgetragene Überlegungen weisen darauf hin, dass Perchlorat als eine Verunreinigung von Dünger vorliegen kann; dies hat zu Besorgnis in der Düngerindustrie geführt. Die vorliegende Untersuchung weist auf Methoden hin, die einer Verbesserung der HPLC-Analyse von Perchlorat dienen; die Methode wurde zur Untersuchung von 15 US-Düngern verwendet. Extraktion mit 50 mM NaOH erwies sich als besser geeignet als eine Extraktion mit Wasser und erhöhte die Extraktionsleistung von 84 auf 98%. Die Vermischung von $\text{Ca}(\text{HO})_2$ in das Extraktionsmedium um 1 : 0,5 oder 1,1 $\text{SO}_4^{2-} : \text{CA}^{+2}$ molare Verhältnisse zu erreichen, reduzierte die analytische Störung, die durch SO_4^{2-} als Folge der Neigung des SO_4^{2-} peaks verursacht wird, um $\approx 75\%$. In den Untersuchungen wurde kein Perchlorat gefunden.

Acknowledgements

The author is grateful to Robin Montenieri for expert technical assistance. Trade name use in the text is included for the convenience of the reader and such inclusion does not constitute a preferential endorsement of the product named over similar products available on the market.

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